

REPORT DOCUMENTATION PAGE			Form Approved OMB NO. 0704-0188		
<p>The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA, 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.</p> <p>PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.</p>					
1. REPORT DATE (DD-MM-YYYY) 30-11-2015		2. REPORT TYPE Final Report		3. DATES COVERED (From - To) 1-Sep-2011 - 31-Aug-2015	
4. TITLE AND SUBTITLE Final Report: Role of Chain Microstructure and Branching on Solution and Thin Film Phase Behavior			5a. CONTRACT NUMBER W911NF-11-1-0417		
			5b. GRANT NUMBER		
			5c. PROGRAM ELEMENT NUMBER 611102		
6. AUTHORS S. Michael Kilbey II			5d. PROJECT NUMBER		
			5e. TASK NUMBER		
			5f. WORK UNIT NUMBER		
7. PERFORMING ORGANIZATION NAMES AND ADDRESSES University of Tennessee at Knoxville 1534 White Avenue Knoxville, TN 37996 -1529			8. PERFORMING ORGANIZATION REPORT NUMBER		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS (ES) U.S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211			10. SPONSOR/MONITOR'S ACRONYM(S) ARO		
			11. SPONSOR/MONITOR'S REPORT NUMBER(S) 59668-CH.15		
12. DISTRIBUTION AVAILABILITY STATEMENT Approved for Public Release; Distribution Unlimited					
13. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.					
14. ABSTRACT This study has focused on elucidating links between topological design of block copolymers and chain stiffness, their assembly in solution and organization in thin films. Novel aspects include the ability to tune chain rigidity without altering chemical composition and precision control of copolymer architecture. Although difficulties in polymer synthesis persisted throughout the project, the phase behavior of topologically complex and semiflexible block copolymers have been examined in solution and thin. Outcomes from those studies provide key insights into how topological and microstructural variations affect assembly and properties. In addition, studies of the solution					
15. SUBJECT TERMS block copolymers, anionic polymerization, thin films, phase behavior, self-assembly					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT UU	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON S. Kilbey
a. REPORT UU	b. ABSTRACT UU	c. THIS PAGE UU			19b. TELEPHONE NUMBER 865-974-4303

Report Title

Final Report: Role of Chain Microstructure and Branching on Solution and Thin Film Phase Behavior

ABSTRACT

This study has focused on elucidating links between topological design of block copolymers and chain stiffness, their assembly in solution and organization in thin films. Novel aspects include the ability to tune chain rigidity without altering chemical composition and precision control of copolymer architecture. Although difficulties in polymer synthesis persisted throughout the project, the phase behavior of topologically complex and semiflexible block copolymers have been examined in solution and thin. Outcomes from those studies provide key insights into how topological and microstructural variations affect assembly and properties. In addition, studies of the solution phase behavior of highly branched star-like copolymers revealed a new and unusual phase segregated morphology, which was linked to the unusual solution assembly behavior of those topologically-constrained stars. Finally, the synthesis of a new class of polymers based on benzofulvene monomer was advanced, a variety of additives were tested for their ability to impart microstructural control, and impacts on macromolecular and thermomechanical properties investigated.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

<u>Received</u>	<u>Paper</u>
05/27/2015 8.00	Wenwen Wang, Weiyu Wang, Hui Li, Xinyi Lu, Jihua Chen, Nam-Goo Kang, Qiuyu Zhang, Jimmy Mays. Synthesis and Characterization of Graft Copolymers Poly(isoprene-, Industrial & Engineering Chemistry Research, (02 2015): 0. doi: 10.1021/ie504457e
05/27/2015 10.00	Xu Wang, Jesse L. Davis, Juan Pablo Hinestrosa, Jimmy W. Mays, S. Michael Kilbey. Control of Self-Assembled Structure through Architecturally and Compositionally Complex Block Copolymer Surfactant Mixtures, Macromolecules, (10 2014): 0. doi: 10.1021/ma5012667
05/27/2015 9.00	Wenwen Wang, Weiyu Wang, Xinyi Lu, Sachin Bobade, Jihua Chen, Nam-Goo Kang, Qiuyu Zhang, Jimmy Mays. Synthesis and Characterization of Comb and Centipede Multigraft Copolymers P, Macromolecules, (11 2014): 0. doi: 10.1021/ma501866t
09/03/2014 3.00	Dawen Li, Jimmy W. Mays, S. Michael Kilbey II, Jihua Chen, Jose Alonzo, Xiang Yu, Kunlun Hong, Jamie M. Messman, Ilia Ivanov, Nickolay Lavrik, Moloy Banerjee, Rajendra Rathore, Zhenzhong Sun. Grafting-Density Effects, Optoelectrical Properties and Nano-Patterning of Poly(para-Phenylene) Brushes, J Materials Chemistry A, (09 2013): 13426. doi:
09/19/2013 6.00	Juan Pablo Hinestrosa, David Uhrig, Deanna L. Pickel, Jimmy W. Mays, S. Michael Kilbey II. Hydrodynamics of polystyrene-polyisoprene miktoarm star copolymers in a selective and a non-selective solvent, Soft Matter, (08 2012): 10061. doi:
11/23/2015 12.00	Kamlesh Bornani, Xu Wang, Jesse L. Davis, Xiaojun Wang, Weiyu Wang, Juan Pablo Hinestrosa, Jimmy W. Mays, S. Michael Kilbey II. Impact of chain microstructure on solution and thin film self-assembly of PCHD-based semi-flexible/flexible diblock copolymers, Soft Matter, (07 2015): 6509. doi: 10.1039/C5SM01245G
TOTAL:	6

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received Paper

TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

Kilbey, S. M. II “Interface and Thin Film Engineering: Chemical and Material Approaches for Tailoring Self-Assembly, Structure and Properties”, invited presentation given at Honeywell FM&T NSC. Kansas City, MO. July 2015.

Kilbey, S. M.; Bornani, K.; Wang, X.; Davis, J. “Impact of Chain Microstructure on the Properties and Self-assembly of Poly(1,3-cyclohexadiene)-based Diblock Copolymers”, to be presented at the 2015 National Meeting of the American Institute of Chemical Engineers. Salt Lake City, UT. November 2015.

Number of Presentations: 0.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received

Paper

08/28/2014 7.00 Wenwen Wang, Weiyu Wang, Xinyi Lu, Jihua Chen, Nam-Goo Kang, Qiuyu Zhang, Jimmy Mays. Synthesis and Characterization of Comb Graft Copolymers Poly(isoprene-g-styrene) of High Molecular Weight by a Combination of Anionic Polymerization and Free Radical Emulsion Polymerization, Polymer Chemistry (06 2014)

08/28/2014 5.00 Jesse Davis,, Juan Pablo Hinestrosa, Jimmy Mays, Xu Wang, S. Michael Kilbey II. Control of Self-Assembled Structure through Architecturally- and Compositionally-Complex Block Copolymer Surfactant Mixtures, Macromolecules (06 2014)

11/23/2015 14.00 Jesse L. Davis, Xu Wang, Kamlesh Bornani, Juan Pablo Hinestrosa, Jimmy W. Mays, S. Michael Kilbey, II. Solution Properties of Architecturally Complex Multiarm Star Diblock Copolymers in a Non-selective and Selective Solvent for the Inner Block, Macromolecules (11 2015)

TOTAL: 3

Number of Manuscripts:

Books

Received

Book

TOTAL:

Received

Book Chapter

TOTAL:

Patents Submitted

Patents Awarded

Awards

PI Kilbey was elected at Chair of the Materials Engineering and Sciences Division of the American Institute of Chemical Engineers

Graduate Students

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	Discipline
Kamlesh Bornani	0.75	
Jesse Davis	0.25	
FTE Equivalent:	1.00	
Total Number:	2	

Names of Post Doctorates

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Names of Faculty Supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	National Academy Member
S. Michael Kilbey II	0.00	
Jimmy W. Mays	0.00	
FTE Equivalent:	0.00	
Total Number:	2	

Names of Under Graduate students supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):..... 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:..... 0.00

Names of Personnel receiving masters degrees

NAME

Total Number:

Names of personnel receiving PHDs

NAME

Weiyu Wang

Jesse Davis

Total Number: 2

Names of other research staff

NAME

PERCENT SUPPORTED

FTE Equivalent:

Total Number:

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

See Attachment

Technology Transfer

During the past year we visited Army Research Laboratory, learning advanced electron microscopy imaging techniques and sharing protocols of sample preparation methodologies we have developed during the course of this program.

(4) Scientific Progress and Accomplishments

Role of Chain Microstructure and Branching on Solution and Thin Film Phase Behavior

PI: S. Michael Kilbey II

Co-PI: Jimmy W. Mays

Performing Organization: University of Tennessee, Knoxville, TN 37996

ARO Proposal No: 59668-CH

Summary of the Project and Key Research Outcomes

The overarching goal of this research project was to understand how the design of conformationally-complex copolymers affects their organization in solution and in thin films, focusing particularly on multi-arm star copolymers having branched topologies and tailored chain microstructure. Key aspects of the research include the ability to independently tune chain stiffness of polymers based on 1,3-cyclohexadiene through control of chain microstructure and also to control polymer topology using various linking strategies to tailor the number of arms of each type. The ability to decouple the role of chain stiffness from the impact of polymer architecture remains a novel feature that distinguishes this research effort. Beyond the fundamental importance of the research propositions, this work impacts applications that require high-performance polymers that have properties found in rigid and semiflexible chains, such as high glass transition temperatures, thermal stability and high mechanical strengths.

One of the two main lines of research hinges on tailoring chain rigidity by controlling the microstructure of poly(1,3-cyclohexadiene) (PCHDs) blocks of copolymers. Maintaining polymer chemistry constant while generating semiflexible polymers with systematic variation in chain stiffness is compelling and novel, but it also presses against two well-known challenges: there are known issues with the polymerizability of 1,3-cyclohexadiene, and polymers that are mechanically tough are often insoluble, which limits their processability and stability during synthesis. Despite these challenges and with two full years devoted to synthesis via anionic methods as well as by various chain coupling reactions, we were ultimately successful in producing one particular set of microstructurally-tailored copolymers, and studies of their solution and thin film phase behaviors allowed us to deliver new understandings of how chain persistence, controlled through microstructure, affects behaviors. *Our efforts delivered deeper insights into the role of initiator design and additive on polymerizability of 1,3-cyclohexadiene and mechanisms of monomer addition in poly(1,3-cyclohexadiene)s, and our results challenge standard notions of the direct link between persistence length and chain rigidity.* Also in the course of the project, we developed useful chemistries for modifying surfaces with PCHD chains and explored relationships between deposition, nanoscale structure, and interfacial properties.

The other major area of the project focused on topologically complex block copolymers based on centrosymmetric star copolymers. We synthesized and examined solution behaviors of 4-arm and 8-arm miktoarm star copolymers based on poly(styrene) and poly(isoprene), PS/PI stars, and we also examined the solution structure of more highly constrained diblock copolymer stars having (on average) 26 and 40 arms, with each arm consisting of a diblock copolymer of PS-block-poly(2-vinylpyridine). *Our work is additive to a body of knowledge that elucidates links between topology and star copolymer design and dynamics and structure in solution. An outstanding outcome of our work in this area is the elucidation of an unusual solution morphology adopted by highly branched star block copolymers in solution.* This structure is consistent with our studies demonstrating the tendency of those block copolymers to remain

isolated as unimers in solution even at concentrations exceeding overlap. This finding alters conventional thinking about how structures of topologically-complex block copolymers in solution are represented. Moreover, these findings were enabled by the development of new and useful strategies for preparing samples of solvated block copolymers for imaging by transmission electron microscopy. Imaging polymeric structures formed in organic solution is a well-known challenge because solvent volatility makes preparation of ultrathin films (less than 100 nm) that are transmissive to electrons especially difficult. Thus, our methodologies are expected to be welcomed as useful and powerful.

Finally, because of the difficulties encountered with anionic polymerization of 1,3-cyclohexadiene and cross-over to create an elaborate suite of block copolymers, including branched materials, we worked to develop anionic polymerization of benzofulvene monomer with microstructure control. This monomer exhibits excellent polymerizability by anionic methods and a variety of additives were tested to control chain microstructure. In addition, the smooth crossover to create block copolymers containing isoprene monomers appears to be a promising route to develop thermoplastic elastomers with properties that transcend traditional styrene/butadiene thermoplastic elastomers. Similarly, a new method that combines free radical emulsion polymerization of macromonomers was used to create topologically-complex graft copolymers. *These advances are significant because they broaden the range of novel copolymers that can be made, including flexible/semiflexible block copolymers, and widen the window of materials/property space.*

In total and as will be captured in the following subsections that delve into the most significant outcomes, *this project yielded important advances in polymer chemistry, imaging of soft matter structures, and physical behaviors of novel macromolecular materials.* Insights into the role of branching and chain stiffness on solution assembly and thin film structure and properties have been delivered. Synthetic efforts have illuminated new routes to tailored, complex polymers and copolymers and yielded relationships between synthetic conditions and macromolecular properties. The fundamental knowledge generated from these efforts not only fills key gaps in knowledge, but it is reasonable to expect that outcomes from this research program will inform efforts to use rigid and tough polymeric materials or highly branched block copolymers to solve particular materials challenges.

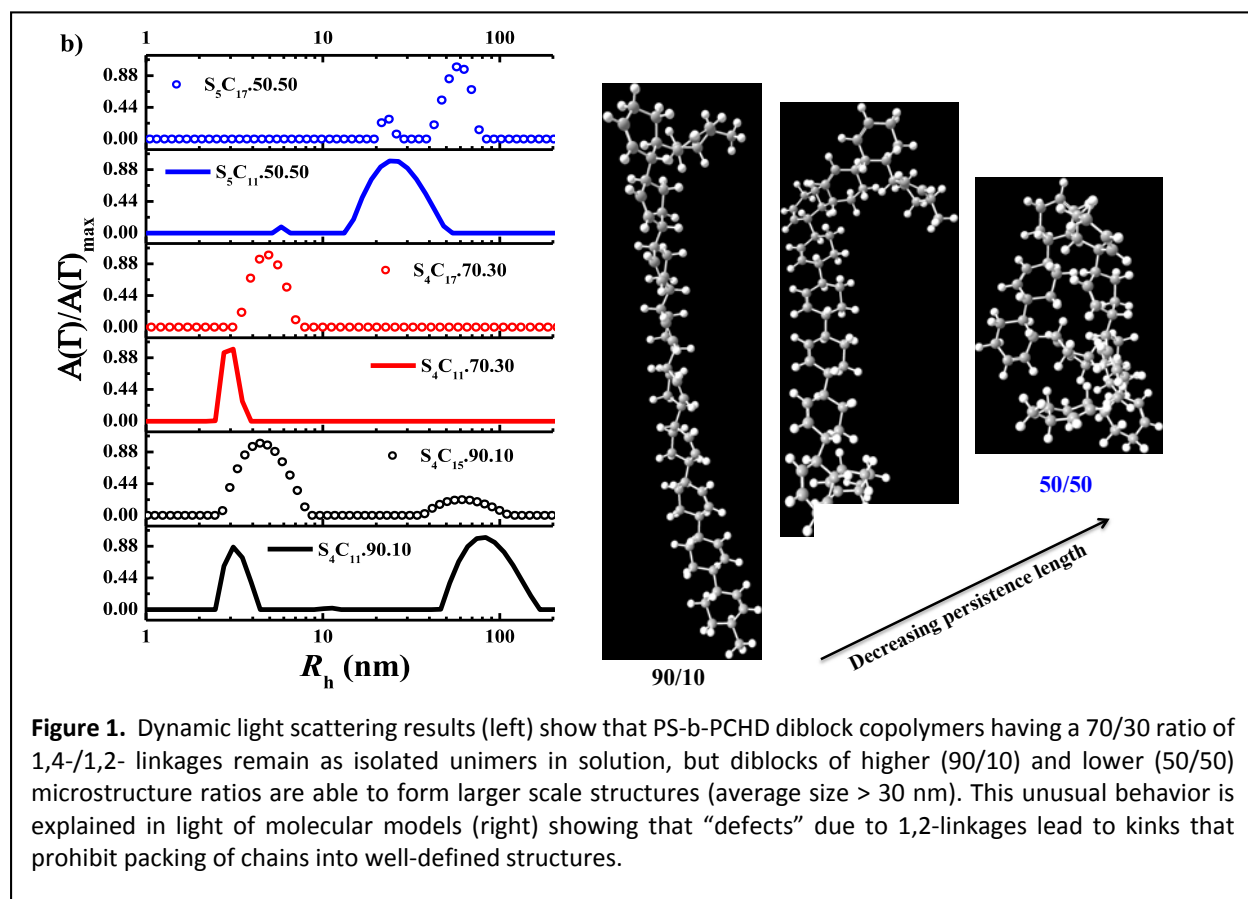
Highlighted Research Accomplishments:

A. Role of Chain Microstructure on Organization of Flexible/Semiflexible Block Copolymers

The choice of 1,3-cyclohexadiene as the tailorable monomer was motivated by the knowledge that polar additives influenced the microstructure of poly(1,3-cyclohexadiene) (PCHD) polymers by controlling the relative amount 1,4 linkages or 1,2 linkages. These microstructural changes affect the thermo-mechanical properties of the copolymers, with higher 1,2 content leading to “stiffer” materials. Beyond the successful syntheses of a series of poly(styrene)-b-PCHD copolymers having systematic variation in chain microstructure and PCHD block molecular weights, efforts to overcome known issues with 1,3-cyclohexadiene to create multiblock copolymers were heroic but unsuccessful: At least 20 different approaches to making multiblock and heteroarm star copolymers involving different initiators, protected initiators, and end-capping reactions followed by post-polymerization coupling strategies (including orthogonal reactions) were attempted; unfortunately none were successful. As reported in our Year 3 report, all of these attempts resulted in extremely poor yields, mixed products, or ill-defined polymers.

Nevertheless, the PS-b-PCHD diblock copolymers were used to examine how microstructure impacts solution and thin film structure. Specifically, using a combination of dynamic light scattering and

transmission electron microscopy (TEM) imaging, we proved how the chain repeat unit design, which is a nanoscale structural element, impacts organization in a selective solvent. Notably, our work shows that “defects” caused by 1,2-linkages creates a window where the chains are unable to self-organize into large ensembles. Rather than suffer packing imperfections, and as summarized and depicted in Figure 1, the chains prefer to remain as isolated unimers in solution. As described in our 2015 publication in *Soft Matter*, this preference impacts their thin film structure as well. This finding of “microstructure controlled” behavior is distinctive not only because it has never been observed before, but because it provides a clear demonstration that the ability to tailor the nanoscale conformational design manifests in unusual solution and thin film structures. This finding is especially compelling in view of the fact that a stated goal of nanotechnology is to harness the ability to control materials at the nanoscale to dictate structure and properties at larger length scales (up to macroscale). These findings also challenge our interpretation that rigid (stiff) polymers have large persistence lengths: by thermal measurements, increasing 1,2 content produces tougher, more thermally-stable materials; however, and as intimated by the molecular models shown in Figure 1, as 1,2 content increases, the persistence length decreases because the bonding configuration causes the chain to double back upon itself. Although we have some disappointment that challenges in synthesis tempered the quantity of different copolymer designs we were able to study, we are confident that these findings are of a depth and significance that ultimately will move the field.



B. Solution Phase Morphology and Advances in TEM Imaging of Topologically Complex Copolymers.

Our efforts to characterize the solution phase behavior of topologically complex block copolymers relied mainly on dynamic light scattering, which provides insight into the population of scatterers and their size

distribution(s), and TEM imaging, which provides insight into real-space structure. Using a series of centrosymmetric PS_nPI_n star copolymers with $n = 1$ (diblock), 2 (4-arm mikto-arm star), and 4 (8-arm mikto-arm star), we explored how systematic variations in both the number of arms and polymer composition affects the ability of the stars to assemble in solution, and connected those behaviors to thin film structures. While PS/PI diblock copolymers are one of most widely studied copolymer systems, topological constraints present in non-linear architectures may impose structural restrictions that distinguish behaviors of branched block copolymers from their linear diblock copolymer analogs.

With this in mind, we investigated the microphase segregation behavior of a series of PS_nPI_n star copolymers in hexane, which is a solvent that is strongly selective for the PI blocks. (Hexane is a good solvent for PI; non-solvent for PS.) The particular polymers studied are presented in **Table 1** below. Our results show that all of the polymers, regardless of composition for micellar structures in solution, with the primary difference manifesting in size controlled by the PI block size: in general, doubling the size of the well-solvated PI block doubles the size of the aggregate produced by self-assembly. The ability of the $n = 4$ structures to self-assemble is somewhat surprising, given that microphase segregation into micelles requires that the chains of these heteroarm star copolymer separate the macromolecule into two distinct halves, with PI chains occupying one side while PS chains occupy the other half. However, this highly constrained structure is consistent with light scattering results.

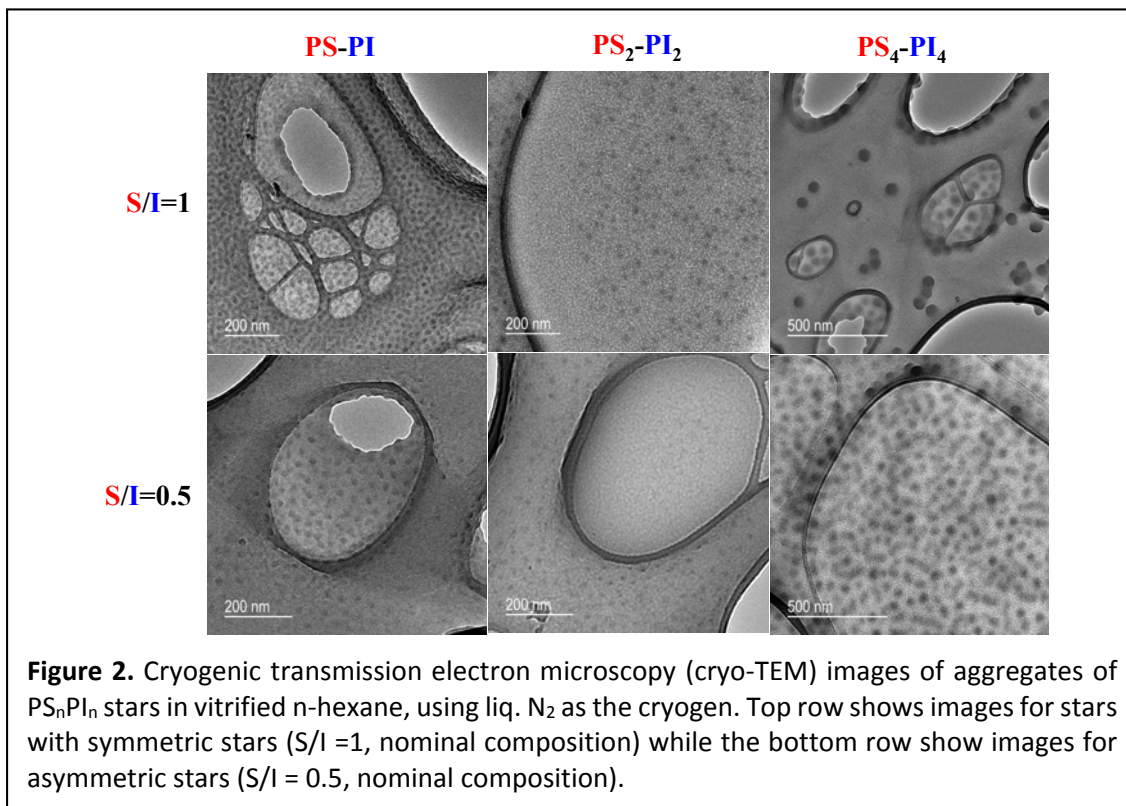
Table 1. Molecular properties of PS_nPI_n copolymers, with $n = 1$ (diblock), 2 and 4 (mikto-arm stars).

Polymer	Target M_n	Actual M_n	PDI	Composition	
				f_{PS}	PS:PI
PS - PI	15k-15k	16.9k-16.3k	1.04	0.509	1.0:1
	15k-30k	16.9k-30.3k	1.03	0.358	0.56:1
$PS_2 - PI_2$	30k-30k	28.6k-30.9k	1.07	0.480	0.93:1
	30k-60k	34.6k-74.8k	1.06	0.316	0.46:1
$PS_4 - PI_4$	60k-60k	62.9k-74.8k	1.07	0.457	0.840:1
	60k-120k	62.9k-116.8k	1.06	0.350	0.54:1

To verify our inferences from light scattering, we worked incredibly hard to develop the ability to image the native structures in solution using transmission electron microscopy (TEM). To appreciate the challenge this represents, it is instructive to consider that TEM imaging requires the film to be extremely thin, on the order of 50 nm, in order to be transmissive to a collimated electron beam. To the best of our knowledge, no one has been successful in imaging soft matter aggregates in n-hexane, ostensibly because the extremely high vapor pressure makes it impossible to create a thin (50 nm) film that spans the holes of a lacey carbon grid that is used in TEM imaging: the film evaporates before it can be vitrified. We developed a protocol that overcame this challenge. By precooling the solution and grids, we were able to cast films on lacey carbon grid (mesh size of 200), blot and vitrify them at -175 °C using liquid nitrogen as the cryogen. Using this procedure, we were able to image the micellar aggregates of the PS_nPI_n star copolymers in hexane, as shown in **Figure 2**. The TEM images confirm that the aggregates are spherical in shape and sizes are consistent with trends observed in light scattering studies. We also examined differences between solution and thin film structures imaged via atomic force microscopy, explaining microstructural reorganizations based on strength of intermolecular microphase segregation.

While the aforementioned challenges in synthesis of semiflexible block copolymers based on PCHD prevented us from synthesizing and studying nonlinear (star-like) block copolymers containing both flexible and semiflexible chains, we believe that the protocols we developed for imaging microphase segregated structures will be appreciated by the wider community. It represents a new and useful method

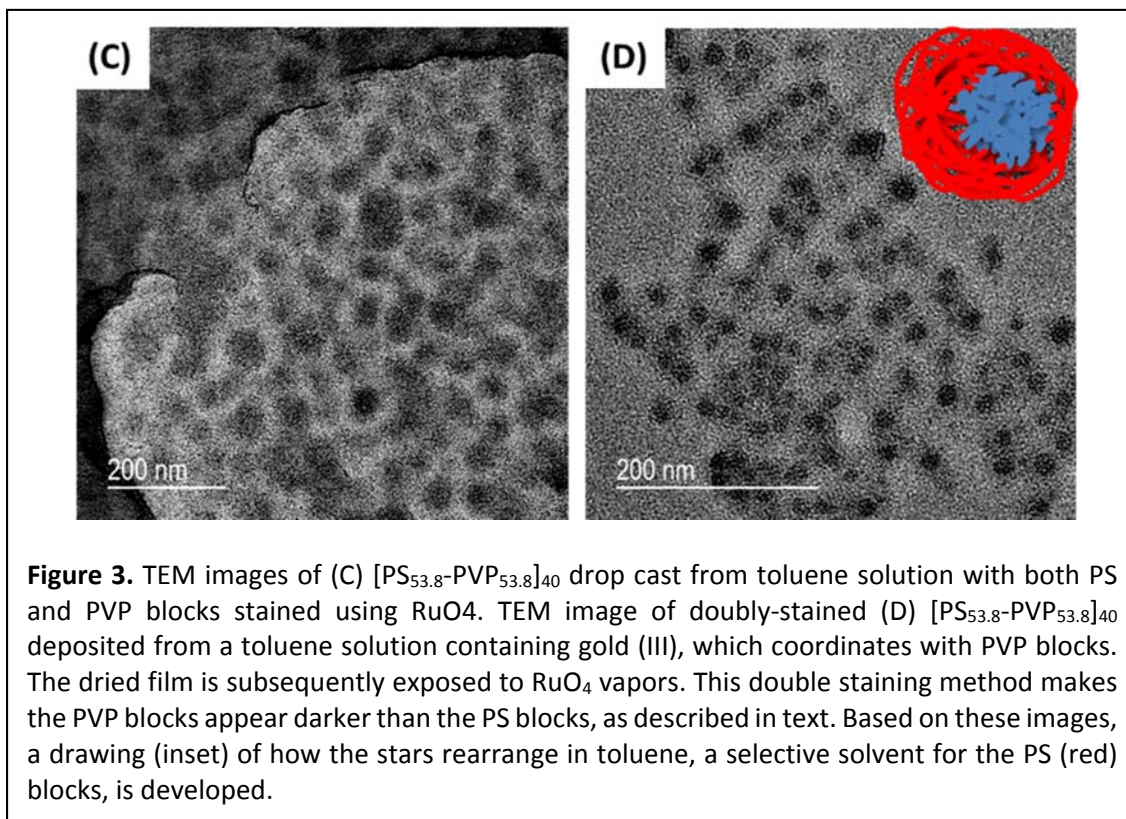
that may be brought to-bear to image nanoscale structure of other polymer systems in volatile organic solvents.



Along these lines, we have used adaptations of these methods to resolve the solution morphology of other highly branched star block copolymers, gaining insight into how a dense topology affects microphase segregation. Our work reveals a new and unexpected morphology in 40-arm star block copolymers in which each arm is a poly(2-vinylpyridine)-*block*-polystyrene diblock copolymer. As described in our recently submitted manuscript and captured in **Figure 3**, we were able to prepare films suitable for TEM imaging and use a double staining technique to allow PVP domains to be distinguished from the PS domains. The TEM image shown on the left in **Figure 3** (labelled as (C)) employed RuO_4 staining, which indiscriminately stains both blocks. This allows the overall structure to be deduced, but reveals nothing about the microstructure. On the other hand, to produce the image on the right (labelled as (D)) we used a sequential staining of RuO_4 , and $Au(III)$, which allows the microphase segregated structure to be resolved because the dual staining renders the PVP blocks darker than the PS blocks (due to the reduction of gold ions associated with PVP blocks by the electron beam during exposure). In this image, the lighter regions that surround the PVP domains are the RuO_4 stained PS blocks (lighter because they are stained by RuO_4 only). It is seen that the PVP end blocks collapse and aggregate within a region of the star, while the PS blocks stretch to remain in contact with the solution. In so doing, the PS chains shield the PVP blocks from the solvent, forming a type of asymmetric structure that is depicted in the inset cartoon.

This represents a powerful and compelling finding that simultaneously advances our understanding of the structural behavior of topologically constrained block copolymers and challenges current understanding of these systems. Conceptually, it might be reasonable to expect that the poorly solvated, outer PVP blocks that are at the periphery of star would simply collapse upon their contour length, segregating at

the PS/PVP interface, or possibly bury themselves within the star, either individually or by clustering with a few PVP blocks from neighboring chains, as ways to minimize contact with toluene. However, both of these possibilities would lead to more unfavorable contacts between PVP segments and either PS segments or solvent toluene than if multiple PVP blocks were able to “find” each other and segregate themselves from toluene or PS segments. In addition, the structure in which PVP blocks are collapsed but at the periphery of the structure would seem to invite multi-star aggregation, which was not seen in our light scattering studies (or in other TEM images, both of which are not shown here for brevity). Thus, the type of structure implied by image produced using dual staining (**Figure 3D**) and depicted in the inset cartoon would allow the stars, particularly those with long PVP blocks, to remain isolated due to repulsive intermolecular interactions between the well-solvated PS blocks that shield the PVP domain. This structural behavior also would seemingly lead to reduced frictional interactions between the stars. Not only does the identification of a segregated morphology driven by intramolecular microphase separation that result in PVP blocks collapsing and in the inner region seems surprising given the high level of geometric constraint in these star diblock copolymers, but these studies underscore the idea that behaviors of topologically-complex amphiphilic block copolymers differ in unexpected ways from the behaviors of their linear analogs and offer new and unusual structures.



C. New Synthetic Approaches to Topologically- and Microstructurally-Complex Copolymers

Despite challenges with anionic polymerization of PCHD based materials, our project has yielded advances in the preparation of topologically- and microstructurally-complex copolymers. In particular, free radical emulsion polymerization of isoprene monomer and polystyrene macromonomers proved to be a successful approach for making very high molecular weight poly(isoprene)-*graft*-poly(styrene) (PS-*g*-PI) block copolymers. This approach is advantageous because it broadens the choice of solvents (dispersing phase) that can be used. In addition, due to challenges with preparation of PCHD based materials, we

studied anionic polymerization of benzofulvene, a conjugated diene monomer that is a planar cyclic analog of 2-phenyl-1,3-butadiene, which possesses characteristics of 1,3-butadiene and styrene, which are very well-behaved monomers in anionic polymerization. The role of additives that tailor chain microstructure was investigated, delivering new insights into relationships between polymerization conditions (additive type, additive-to-initiator ratio), molecular weight characteristics, and thermomechanical properties, as shown in **Table 2**.

Table 2. Anionic Polymerization of benzofulvene in the presence of additives.

Sample ID ^a	[Additive] [Initiator]	M _n (kg/mol)		M _w /M _n	Yield (%)	T _g (°C)
		Calc'd	Obs'd			
PBF_DME_16	10	16.3	15.9	1.10	99%	191.5
PBF_DME_40	10	40.0	39.0	1.12	98%	198.7
PBF_DABCO_20	3	20.3	28.5	1.86 ^e	86%	187.0
PBF_TMEDA_20	1	19.8	12.2	2.35 ^e	12%	155.2
PBF_ <i>sec</i> -BuOLi_7	10	7.3	6.9	1.16	99%	142.3
PBF_ <i>sec</i> -BuOLi_23	10	22.7	23.1	1.10	99%	153.1

^aAdditives tested include dimethoxyethane (DME), 1,4-diazabicyclo[2.2.2]octane (DABCO) or tetramethylethylenediamine (TMEDA) with *n*-BuLi initiator, and *sec*-BuOLi (lithium *sec*-butoxide) with *sec*-BuLi as initiator.

This work on benzofulvenes was extended to produce diblock copolymers of poly(isoprene)-block-poly(benzofulvene) (PI-*b*-PBF) and PBF-*b*-PI-*b*-PBF triblock copolymers, which appear to have intriguing properties as thermoplastic elastomers due to their combination of hard/soft/hard blocks. These materials were fully characterized by NMR and size exclusion chromatography to determine chain properties, including microstructure of isoprene and benzofulvene repeat units and molecular weights, respectively. These copolymers are complex materials because monomer addition of benzofulvene can be 1,2 or 1,4, and isoprene monomer can add by either 1,4 or 3,4 addition, as suggested by **Figure 4.**, and microstructure impacts thermomechanical properties, as evident from data shown in **Table 2**. Finally, we also studied the effect of partial and complete hydrogenation on the thermal stability, mechanical and morphological properties of PBF-*b*-PI-*b*-PBF triblock copolymers. Thermal stability was greatly improved by both partial and complete hydrogenation; the glass transition temperature (T_g) of fully hydrogenated PBF dropped to 130 °C and and mechanical properties such as ultimate stress also were greatly improved compared to the parent copolymers. Manuscripts based on these recent findings are in preparation.

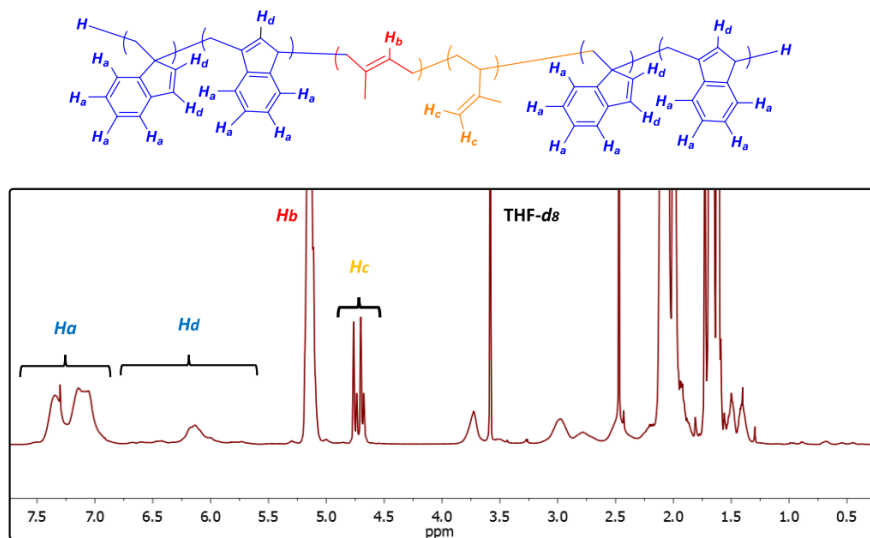


Figure 4. The microstructure of PBF-*b*-PI-*b*-PBF triblock copolymers is revealed through ¹H-NMR spectroscopy studies of the copolymers in THF-*d*₈.